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Advanced Synthesis & Catalysis

Supporting Information

Highly Enantioselective Copper-Catalyzed Allylic Alkylation with Phosphoramidite Ligands

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General Remarks: All solvents were reagent grade and were dried and distilled before use. All solvents were stored under nitrogen. All reactions were carried out under argon atmosphere using dried glassware (standard Schlenk procedures). Chromatography: silica gel Merck Type 9385 230-400 mesh, TLC: silica gel 60, Merck, 0.25 mm. Optical rotations were measured on a Perkin-Elmer 241 MC (at RT). Mass spectra (HRMS) were recorded on an AEI MS-902. HPLC analyses were performed on a Water 480 with a LC spectrophotometer or a Water 600E system controller with a Waters 991 photodiode array detector using different chiral columns specified where necessary. ^{1}H-NMR, ^{13}C-NMR and ^{31}P-NMR spectra were recorded on a Varian Gemini-200 (50.32 MHz), Varian 300 (75.48 MHz) or Varian 500 (125.80 MHz) spectrometer in $CDCl_3$. Chemical shift values are denoted in δ-units (ppm) relative to residual solvent peaks ($CHCl_3$, δ = 7.24 ppm for protons, δ = 77 ppm for carbon atoms and H_3PO_4, δ = 0.0 ppm for phosphorus atoms). GC measurements were performed either on a HP 5890 A, HP 5890 series II or a HP6890 gas chromatograph with flame ionization detector using different columns specified where necessary.

Materials: Cinnamyl bromide **1a**, $(CuOTf)_2{\cdot}C_6H_6$ and diethylzinc were purchased from Aldrich and used without further purification. Dibutylzinc in heptane was purchased from Fluka, distilled and used as a toluene solution. Diisopropylzinc was prepared according to literature procedure and used as a toluene solution.[1] Ligands (**4**, **5**, **6**, **10**)[2], (**8**, **9**, **11**, **16**, **17**, **18**)[3], **15**[4], (**19**, **20**, **21**, **22**, **23**)[5] and (**24**, **25**, **26**, **27**, **28**)[6] were prepared according to literature procedures. The spectral data were consistent with those previously reported. Triethylamine was freshly distilled. All secondary amines as well as all other chemicals are commercially available and otherwise synthesised according to literature procedures. (*S*)-BINOL was kindly provided by Dr. Hyett (DSM). Ligands **7**, **12**, **13**, **14** were prepared according to a literature

procedure for related ligands.[2] The substrates **1b**, **1c**, **1e**, **1f** and **1g** were prepared through a modified literature procedure.[7] Substrate **1d** was prepared according to literature procedures.[7,8] If previously reported the spectral data were consistent with those in literature.

(*S*)-3-(4'-Chlorophenyl)-1-pentene (2b). Purification by column chromatography (SiO_2, pentane, R_f = 0.9) gave 95 mg (53%) of a mixture of **2b** and **3b** as a colorless oil. NMR experiments were performed on the mixture of products, but only data of the branched product **2b** are given. ^{1}H-NMR (300MHz) δ = 7.25 (d, *J* = 8.4 Hz, 2H), 7.09 (d, *J* = 8.4 Hz, 2H), 5.88 (m, 1H), 5.00 (m, 2H), 3.10 (dt, *J* = 7.7, 7.3 Hz, 1H), 1.69 (dq, *J* = 7.7, 7.3 Hz, 2H), 0.83 (t, *J* = 7.3 Hz, 3H); ^{13}C-NMR (200 MHz) δ = 142.1, 141.7, 129.0, 128.7, 128.5, 114.4, 51.0, 28.2, 12.0; Ms (EI) for $C_{11}H_{13}Cl$: m/z = 180 $(M)^+$. Determination of the ee of **2b** was performed by GC on a CP-Chiralsil-Dex CB, 25m x 0.25mm column, He-flow 1.0 ml/min., oven temp. 50 °C, rate 10 °C/min., fin. temp. 120 °C, fin. time 30 min., t_r 19.7 min. (minor) t_r 20.2 min. (major).

(*S*)-3-(4'-(Trifluoromethyl)phenyl)-1-pentene (2c). Purification by column chromatography (SiO_2, pentane, R_f = 0.9) gave 116 mg (54%) of a mixture of **2c** and **3c** as a colorless oil. NMR experiments were performed on the mixture of products, but only data of the branched product **2c** are given. ^{1}H-NMR (300MHz) δ = 7.53 (d, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 8.1 Hz, 2H), 5.90 (m, 1H), 5.03 (m, 2H), 3.19 (dt, *J* = 7.7, 7.3 Hz, 1H), 1.73 (dq, *J* = 7.7, 7.3 Hz, 2H), 0.85 (t, *J* = 7.3 Hz, 3H); ^{13}C-NMR (200 MHz) δ = 148.6, 141.2, 128.5 (q, $^2J_{(C,F)}$ = 32 Hz), 128.0, 125.3 (q, $^3J_{(C,F)}$ = 4 Hz), 124.4 (q, $^1J_{(C,F)}$ = 272 Hz), 114.9, 51.6, 28.2, 12.0; Ms (EI) for $C_{12}H_{13}F_3$: m/z = 214 $(M)^+$. Determination of the ee of **2c** was performed by GC on a CP-Chiralsil-Dex CB, 25m x 0.25mm column, He-flow 1.0 ml/min., oven temp. 50 °C, rate 10 °C/min., fin. temp. 120 °C, fin. time 30 min., t_r 11.4 min. (minor) t_r 11.8 min. (major).

(*S*)-3-(4'-Nitrophenyl)-1-pentene (2d). Purification by column chromatography (SiO_2, diethyl ether /pentane, 1:49, R_f = 0.6) gave 0.136 g (71%) of a mixture of **2d** and **3d** as a yellow oil. NMR experiments were performed on the mixture of products, but only data of the branched product **2d** are given. ^{1}H-NMR (300MHz) δ = 8.14 (d, *J* = 8.8 Hz, 2H), 7.32 (d, *J* = 8.8 Hz, 2H), 5.89 (m, 1H), 5.06 (m, 2H), 3.25 (dt, *J* = 7.7, 7.3 Hz, 1H), 1.75 (dq, *J* = 7.3, 7.3 Hz, 2H), 0.86 (t, *J* = 7.3 Hz, 3H); ^{13}C-NMR (200 MHz) δ = 152.2, 144.4, 140.4, 128.4, 123.6, 115.5, 51.4, 28.1, 11.9; Ms (EI) for $C_{11}H_{13}NO_2$: m/z = 191 $(M)^+$. Determination of the ee of

2d was performed by GC on a CP-Chiralsil-Dex CB, 25m x 0.25mm column, He-flow 1.0 ml/min., oven temp. 50 °C, rate 10 °C/min., fin. temp. 140 °C, fin. time 80 min., t_r 35.8 min. (minor) t_r 36.5 min. (major).

(*S*)-3-(4'-Methoxycarbonylphenyl)-1-pentene (2e). Purification by column chromatography (SiO_2, ethylacetate /pentane, 1:19, R_f = 0.7) gave 0.169 g (83%) of a mixture of **2e** and **3e** as a colorless oil. NMR experiments were performed on the mixture of products, but only data of the branched product **2e** are given. ^{1}H-NMR (300MHz) δ = 7.95 (d, *J* = 8.1 Hz, 2H), 7.23 (d, *J* = 8.1 Hz, 2H), 5.91 (m, 1H), 5.05-4.99 (m, 2H), 3.88 (s, 3H), 3.18 (m, 1H), 1.73 (m, 2H), 0.84 (t, *J* = 7.3 Hz, 3H); ^{13}C-NMR (200 MHz) δ = 167.1, 149.9, 141.3, 129.8, 128.1, 127.7, 114.8, 52.0, 51.7, 28.2, 12.0; HRMS calcd for $C_{13}H_{16}O_2$ 204.116, found 204.115; Determination of the ee of **2e** was performed by GC on a CP-Chiralsil-Dex CB, 25m x 0.25mm column, He-flow 1.0 ml/min., oven temp. 50°C, rate 10 °C/min., fin. temp. 120 °C, fin. time 90 min., t_r 66.0 min. (minor) t_r 67.6 min. (major).

(*S*)-3-(1'-Naphthyl)-1-pentene (2f). Purification by column chromatography (SiO_2, pentane, R_f = 0.8) gave 0.151 g (77%) of a mixture of **2f** and **3f** as a colorless oil. NMR experiments were performed on the mixture of products, but only data of the branched product **2f** are given. ^{1}H-NMR (300MHz) δ = 8.11 (d, *J* = 10.6 Hz, 1H), 7.84 (d, *J* = 7.3 Hz, 1H), 7.70 (d, *J* = 7.7 Hz, 1H), 7.55-7.36 (m, 4H), 6.05 (m, 1H), 5.08 (m, 2H), 3.99 (dt, *J* = 7.3, 7.0 Hz, 1H), 1.90 (dq, *J* = 7.0, 7.3 Hz, 2H), 0.94 (t, *J* = 7.3 Hz, 3H); ^{13}C-NMR (200 MHz) δ = 141.7, 140.4, 134.0, 131.8, 128.9, 126.6, 125.6, 125.5, 125.3, 123.9, 123.4, 114.6, 46.0, 28.0, 12.4; Ms (EI) for $C_{15}H_{16}$: m/z = 196 $(M)^+$. Determination of the ee of **2f** was performed by chiral HPLC: Chiralcel OD, isocratic heptane/2-propanol: 399/1, 1.0 ml/min., λ_{det}: 281 nm., t_r 12.3 min. (minor) t_r 14.2 min. (major).

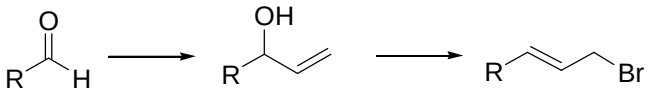
(*S*)-3-(Cyclohexyl)-1-pentene (2g). [9] Purification by column chromatography (SiO_2, pentane, R_f = 0.9) gave 0.087 g (57%) of a mixture of **2g** and **3g** as a colorless oil. NMR experiments were performed on the mixture of products, but only data of the branched product **2g** are given. ^{1}H-NMR (300MHz) δ = 5.58-5.46 (m, 1H), 4.99-4.85 (m, 2H), 1.98-0.86 (m, 14H), 0.80 (t, *J* = 7.3 Hz, 3H); ^{13}C-NMR (200 MHz) δ = 141.5, 114.9, 52.0, 41.5, 31.2, 29.7, 26.7, 24.4, 12.1; Ms (EI) for $C_{11}H_{20}$: m/z = 152 $(M)^+$. Determination of the ee of **2g** was performed by GC on a CP-Chiralsil-Dex CB, 25m x 0.25mm column, He-flow 1.0 ml/min., oven temp.

50 °C, rate 10 °C/min., fin. temp. 75 °C, fin. time 43 min., t_r 42.9 min. (minor) t_r 43.8 min. (major).

(*S*)-3-Phenyl-4-methyl-1-pentene (2h).[10] Purification by column chromatography (SiO_2, ether: pentane, 1: 100) gave 136 mg (85%) of a mixture of **2h** and **3h** as a colorless oil. NMR experiments were performed on the mixture of products, but only data of the branched product **2h** are given. $[\alpha]_D^{22}$ = +104.2° (c = 0.15, $CHCl_3$) with 88% ee. Proof of stereochemistry: literature value $[\alpha]_D^{22}$ = +71.3° (c = 1.5, $CHCl_3$) is assigned to the (*S*) enantiomer with 58% ee.[10] ^{1}H-NMR (200 MHz) δ = 7.29 (m, 5H), 6.04 (m, 1H), 5.10 (m, 2H), 2.93 (t, *J* = 8.9 Hz, 1H), 1.95 (m, 1H), 1.02 (d, *J* = 6.7 Hz, 3H), 0.82 (d, *J* = 6.7 Hz, 3H); ^{13}C-NMR (200 MHz) δ = 144.3, 141.2, 128.3, 127.9, 125.9, 114.9, 58.5, 32.6, 21.0, 20.8; Ms (EI) for $C_{12}H_{16}$: m/z = 160 $(M)^+$. Determination of the ee of **2h** was performed by GC on a CP-Chiralsil-Dex CB, 30m x 0.25mm column, He-flow 1.0 ml/min, isothermic 85°C, t_r 33.2 min: (*R*)-**2h**, t_r 34.3 min: (*S*)-**2h**.

(*S*)-3-Phenyl-1-heptene (2i).[11] Purification by column chromatography (SiO_2, ether: pentane, 1: 50, Rf = 0.8) gave 118 mg (55%) of a mixture of **2i** and **3i** as a colorless oil. NMR experiments were performed on the mixture of products, but only data of the branched product **2i** are given. $[\alpha]_D^{22}$ = +44.3° (c = 0.12, $CHCl_3$) with 88% ee. ^{1}H-NMR (200 MHz) δ = 7.21 (m, 5H), 5.95 (m, 1H), 5.01 (m, 2H), 3.32 (q, *J* = 7.5 Hz, 1H), 1.70 (q, *J* = 7.4 Hz, 2H), 1.39-1.02 (m, 4H), 0.87 (t, *J* = 7.0 Hz, 3H); ^{13}C-NMR (200 MHz) δ = 144.7, 142.5, 128.4, 127.6, 126.0, 113.8, 49.9, 35.1, 29.7, 22.6, 14.0; HRMS calcd for $C_{13}H_{18}$ 174.142, found 174.141; Determination of the ee of **2i** was performed by GC on a CP-Chiralsil-Dex CB, 25m x 0.25mm column, He-flow 1.0 ml/min, oven temp.: 70°C, initial time: 70 min., rate: 0.5°C/min., final temp.: 80°C, final time: 50 min, t_r 125.0 min. (minor), t_r 127.6 min. (major).

Synthesis of allylic bromides (1b,1c,1e,1f,1g):



General procedure for the preparation of allylic alcohols: [7] Under an Ar-atmosphere a solution of 25 mmol of aldehyde in THF (30 ml) was added to a cooled solution (0°C) of vinylmagnesium bromide in THF (1M) (30 ml) over a period of 10 min. The reaction mixture was allowed to warm to room temperature, poured into NH_4Cl (aq) (30 ml) and extracted three times with diethyl ether (30 ml). The combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo*.

1-(4'-Chlorophenyl)-allylalcohol. [12] Purification by column chromatography (SiO_2, pentane/ether, 3:1) gave 1.89 g (45%) of the allylic alcohol as a colorless oil. ^{1}H-NMR (300MHz) δ = 7.30 (m, 4H), 5.98 (m, 1H), 5.32 (dd, *J* = 17.2, 1.1 Hz, 1H), 5.21-5.16 (m, 2H), 1.98 (s, OH); ^{13}C-NMR (200 MHz) δ = 140.9, 139.8, 133.4, 128.6, 127.7, 115.6, 74.7; Ms (EI) for C_9H_9ClO: m/z = 168 $(M)^+$.

1-(4'-(Trifluoromethyl)phenyl)-allylalcohol. [12] Purification by column chromatography (SiO_2, pentane/ether, 5:1) gave 2.12 g (42%) of the allylic alcohol as a colorless oil. ^{1}H-NMR (300MHz) δ = 7.60 (d, *J* = 8.1 Hz, 2H), 7.48 (d, *J* = 8.1 Hz, 2H), 6.00 (m, 1H), 5.40-5.19 (m, 3H), 2.01 (d, *J* = 3.7 Hz, OH); ^{13}C-NMR (200 MHz) δ = 146.3, 139.6, 129.5, 126.5, 125.5, 121.4, 116.1, 74.8; Ms (EI) for $C_{10}H_9F_3O$: m/z = 202 $(M)^+$.

3-(4'-Nitrophenyl)-prop-2-en-1-ol. [8,13] 3-(4'-Nitrophenyl)-propenal (9.8 g, 55 mmol) was dissolved in hot 96 % ethanol (750 ml) and heated to 50 °C. To this solution sodium borohydride (0.75 g, 20 mmol) in ethanol (35 ml) was added. The mixture was allowed to cool and remain at room temperature for 3h and the small amount of precipitate was filtered. The solution was then acidified with hydrochloric acid until the orange color turned yellow and was concentrated *in vacuo*. The residue was dissolved in chloroform, washed with water, dried with $MgSO_4$, filtered and concentrated *in vacuo* to a small volume. Upon cooling the product precipitated. After filtration, the collected product was washed three times with diethyl ether to give 8.95 g (91%) of the allylic alcohol as a yellow solid. ^{1}H-NMR (300MHz) δ = 8.17 (d, *J* = 8.8 Hz, 2H), 7.49 (d, *J* = 8.8 Hz, 2H), 6.70 (d, *J* = 15.7 Hz, 1H), 6.52 (dt, *J* = 15.7, 5.1 Hz, 1H), 4.39 (dd, *J* = 5.1, 1.5 Hz, 2H), 1.68 (s, OH); ^{13}C-NMR (200 MHz) δ = 146.8, 143.2, 133.6, 128.1, 126.9, 124.0, 63.0; Ms (EI) for $C_9H_9NO_3$: m/z = 179 $(M)^+$.

1-(4'-(Methoxycarbonyl)phenyl)-allylalcohol. [14] (Reaction performed at –78 °C) Purification by column chromatography (SiO_2, pentane/diethyl ether, 2:1, R_f = 0.3) gave 3.12 g (65%) of the allylic alcohol as a yellow oil. ^{1}H-NMR (300MHz) δ = 8.00 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.1 Hz, 2H), 6.00 (m, 1H), 5.37-5.19 (m, 3H), 3.89 (s, 3H), 2.07 (s, OH); ^{13}C-NMR (200 MHz) δ = 166.9, 147.5, 139.6, 129.8, 129.3, 126.1, 115.9, 74.9, 52.1; Ms (EI) for $C_{11}H_{12}O_3$: m/z = 192 $(M)^+$.

1-(1'-Naphthyl)-allylalcohol. [12] Purification by kugelrohr distillation (0.15 mm Hg, 110 °C) gave 3.4 g (74%) of the allylic alcohol as a white solid. ^{1}H-NMR (300MHz) δ = 8.17 (d, *J* = 7.3 Hz, 1H), 7.86 (d, *J* = 8.4 Hz, 1H), 7.79 (d, *J* = 8.1 Hz, 1H), 7.61 (d, *J* = 7.0 Hz, 1H), 7.54-7.43 (m, 3H), 6.24 (m, 1H), 5.93 (m, 1H), 5.44 (dd, *J* = 17.2, 1.1 Hz, 1H), 5.27 (dd, *J* = 10.3, 1.1 Hz, 1H), 2.05 (d, *J* = 2.9 Hz, OH); ^{13}C-NMR (200 MHz) δ = 139.6, 138.0, 133.9, 130.7, 128.8, 128.5, 126.1, 125.6, 125.4, 123.9, 123.7, 115.6, 72.3; Ms (EI) for $C_{13}H_{12}O$: m/z = 184 $(M)^+$.

3-(Cyclohexyl)-allylalcohol. [15] Purification by column chromatography (SiO_2, pentane/diethyl ether, 9:1, R_f = 0.3) gave 2.59 g (74%) of the allylic alcohol as a colorless liquid. ^{1}H-NMR (300MHz) δ = 5.84 (m, 1H), 5.21-5.10 (m, 2H), 3.80-3.85 (m, 1H), 1.80-1.59 (m, 6H), 1.47-1.43 (m, OH), 1.41-1.32 (m, 1H), 1.28-0.90 (m, 4H); ^{13}C-NMR (200 MHz) δ = 139.8, 115.5, 77.7, 43.4, 28.7, 28.3, 26.5, 26.1, 26.0; Ms (EI) for $C_9H_{16}O$: m/z = 140 $(M)^+$.

General procedure for the preparation of allylic bromides: Under an Ar-atmosphere a solution of PBr_3 (0.95 ml, 10 mmol) in pentane (10 ml) was added dropwise to a solution of allylic alcohol (10 mmol) in pentane (50 ml) at –50 °C. After stirring for 30 min, the solution was poured into water (30 ml) and after separation the organic layer was washed three times with water (3 x 30 ml), dried over $MgSO_4$, filtered and concentrated *in vacuo*.

3-(4'-Chlorophenyl)-allylbromide (1b). Purification by column chromatography (SiO_2, pentane/ether, 4:1) gave 1.18 g (51%) of **1b** as a white solid. ^{1}H-NMR (300MHz) δ = 7.29 (m, 4H), 6.58 (d, *J* = 15.8 Hz, 1H), 6.35 (dt, *J* = 15.8, 7.7 Hz, 1H), 4.12 (d, *J* = 7.7 Hz, 2H); ^{13}C-NMR (200 MHz) δ = 134.3, 134.0, 133.2, 128.8, 127.9, 125.8, 33.0; Ms (CI) for $C_9H_8{}^{79}BrCl$: m/z = 230 $(M)^+$; mp = 56.1-56.4 °C (lit.[16] mp = 60-61.5 °C).

3-(4'-(Trifluoromethyl)phenyl)-allylbromide (1c). Purification by column chromatography (SiO_2, pentane) gave 1.14 g (41%) of **1c** as a yellow solid. ^{1}H-NMR (300MHz) δ = 7.57 (d, *J* = 8.1 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 6.66 (d, *J* = 5.8 Hz, 1H), 6.47 (dt, *J* = 15.8, 7.3 Hz, 1H), 4.13 (d, *J* = 7.3 Hz, 2H); ^{13}C-NMR (200 MHz) δ = 139.2, 132.9, 130.0 (q, $^2J(C,F)$ = 32 Hz), 127.8, 126.9, 125.6, 124.0 (q, $^1J(C,F)$ = 272 Hz), 32.4; Ms (EI) for $C_{10}H_8{}^{79}Br\,F_3$: m/z = 264 $(M)^+$; mp = 35.9-36.8 °C.

3-(4'-Nitrophenyl)-allylbromide (1d). [7,17] A solution 3-(4-nitro-phenyl)-prop-2-en-1-ol (1.07 g, 6 mmol) in diethyl ether (20 ml) was saturated with anhydrous hydrogen bromide. After 3h the solution was dried with $MgSO_4$, filtered and concentrated *in vacuo*. Purification by column chromatography (SiO_2, hexane/dichloromethane, 2:1, R_f = 0.4) gave 0.91 g (63%) of **1d** as a yellow solid. ^{1}H-NMR (300MHz) δ = 8.18 (d, *J* = 8.8 Hz, 2H), 7.51 (d, *J* = 8.8 Hz, 2H), 6.69 (d, *J* = 15.7 Hz, 1H), 6.54 (dt, *J* = 15.7, 7.3 Hz, 1H), 4.14 (d, *J* = 7.3 Hz, 2H); ^{13}C-NMR (200 MHz) δ = 142.2, 142.2, 132.1, 129.9, 127.3, 124.0, 31.8; Ms (EI) for $C_9H_8{}^{79}BrNO_2$: m/z = 241 $(M)^+$; mp = 73.2-75.0 °C (lit.[18] mp = 76 °C).

3-(4'-(Methoxycarbonyl)phenyl)-allylbromide (1e). [19] Purification by column chromatography (SiO_2, pentane /dichloromethane, 1:1, R_f = 0.5), gave 1.07 g (42%) of **1e** as a white solid. ^{1}H-NMR (300MHz) δ = 7.98 (d, *J* = 8.1 Hz, 2H), 7.43 (d, *J* = 8.1 Hz, 2H), 6.66 (d, *J* = 15.7 Hz, 1H), 6.48 (dt, *J* = 15.7, 7.7 Hz, 1H), 4.14 (d, *J* = 7.7 Hz, 2H), 3.90 (s, 3H); ^{13}C-NMR (200 MHz) δ = 166.7, 140.2, 133.4, 130.0, 129.7, 127.8, 126.6, 52.1, 32.6; HRMS calcd for $C_{11}H_{11}O_2{}^{79}Br$ 253.994, found 253.994; mp = 116.8-117.4 °C (lit.[19] mp = 119 °C).

3-(1'-Naphthyl)-allylbromide (1f). [20] Purification by column chromatography (SiO_2, ethylacetate /toluene, 1:9, R_f = 0.4) gave 2.12 g (86%) of **1f** as a brown solid. ^{1}H-NMR (300MHz) δ = 8.08 (d, *J* = 7.3 Hz, 1H), 7.89-7.78 (m, 2H), 7.62-7.37 (m, 5H), 6.43 (dt, *J* = 15.4, 7.7 Hz, 1H), 4.26 (d, *J* = 7.7 Hz, 2H); ^{13}C-NMR (200 MHz) δ = 133.5, 133.3, 131.6, 131.0, 128.6, 128.6, 128.2, 126.3, 125.9, 125.5, 124.2, 123.5, 33.4; Ms (EI) for $C_{13}H_{11}{}^{79}Br$: m/z = 246 $(M)^+$; mp = 56.1-58.9 °C (lit.[21] mp = 56-59 °C).

3-(Cyclohexyl)-allylbromide (1g). Purification by column chromatography (SiO_2, toluene) gave 1.01 g (50%) of **1g** as a colorless oil. ^{1}H-NMR (300MHz) δ = 5.74-5.56 (m, 2H), 3.93

(d, *J* = 6.6 Hz, 2H), 1.94 (m, 1H), 1.71-1.61 (m, 5H), 1.27-0.98 (m, 5H); ^{13}C-NMR (200 MHz) δ = 124.1, 123.9, 40.1, 34.0, 30.3, 25.9, 25.8; Ms (EI) for $C_9H_{15}{}^{79}Br$: m/z = 202 $(M)^+$.

General procedure for the preparation of phosphoramidite ligands: To a cooled solution (-60°C) of PCl_3 (270 µl, 3.0 mmol), Et_3N (860 µl, 6.0 mmol), and toluene (5 ml) under an Ar-atmosphere was added a warm solution (60°C) of the diol (3.0 mmol) and toluene (25 ml) in 5 min. After stirring for 2h the reaction mixture was allowed to warm to room temperature and filtered under an Ar-atmosphere. The filtrate was treated at –40°C with the corresponding secondary amine (3 mmol), which had been deprotonated in THF (5 ml) using BuLi (1.6M hexane). After 16h at ambient temperature, the reaction mixture was filtered, concentrated *in vacuo* and purified by chromatography (SiO_2, hexane or pentane: CH_2Cl_2 or ether) to give the pure phosphoramidite as a white amorphous compound. Stripping with CH_2Cl_2 furnished the phosphoramidites as foamy solids.

***O,O'*-(*S*)-(1,1'-dinaphthyl-2.2'-diyl)-*N,N'*-di-(*S,S*)-1-(1'-naphthyl)ethylphosphoramidite (7).** Purification by column chromatography (SiO_2 hexane/ CH_2Cl_2, 5:2, Rf = 0.37) gave 882 mg (46% yield) of **7** as a white foam. $[\alpha]_D$= +240.0° (c = 0.74, $CHCl_3$); ^{1}H-NMR δ = 7.95 (m, 2H), 7.70-7.14 (m, 22H), 7.03 (t, *J* = 7.8 Hz, 2H), 5.45 (m, *J* = 7.5 Hz, 2H), 1.67 (d, *J* = 7.0 Hz, 6H). ^{13}C-NMR (200 MHz) δ = 150.9, 150.7, 149.5, 139.1, 129.0, 133.2, 132.9, 132.7, 131.4, 130.6, 130.5, 130.3, 129.6, 128.4, 128.3, 128.1, 127.1, 127.0, 126.1, 125.8, 125.4, 124.9, 124.8, 124.6, 124.5, 124.2, 123.1, 122.3, 122.0, 121.5, 53.1, 52.8, 23.3, 23.1; ^{31}P-NMR (200 MHz) δ = 153.4; HRMS calcd for $C_{44}H_{34}NO_2P$ 639.233, found 639.233.

***O,O'*-(*S*)-(1,1'-dinaphthyl-2.2'-diyl)-*N*-benzyl-*N'*-(*S*)-1-(1'-naphthyl)ethylphosphoramidite (12).** Purification by column chromatography (SiO_2 pentane/ ether, 30:1, Rf = 0.36) gave 810 mg (47% yield) of **12** as a white foam. $[\alpha]_D$= +240.4° (c = 0.89, $CHCl_3$); ^{1}H-NMR (300 MHz) δ = 8.21–6.99 (m, 24H), 5.16 (q, *J* = 7.0 Hz, 1H), 4.08 (d, *J* = 15.0 Hz, 1H), 3.08 (d, *J* = 15.0 Hz, 1H), 1.83 (dd, *J* = 7.0, 4.0 Hz, 3H). ^{13}C-NMR (500MHz) δ = 150.1, 150.0, 149.5, 139.8, 138.4, 133.7, 132.8, 132.5, 131.4, 131.3, 130.5, 130.2, 130.1, 128.9, 128.5, 128.3, 128.1, 127.8, 127.0, 126.9, 126.7, 126.0, 125.9, 125.6, 125.5, 124.8, 124.5, 124.2, 124.1, 122.5, 122.4, 122.3, 121.6, 52.6, 52.4, 48.5, 48.4, 23.5, 23.2; ^{31}P-NMR (200 MHz) δ = 141.6; HRMS calcd for $C_{39}H_{30}N\,O_2P$ 575.201, found 575.200.

***O,O'*-(*S*)-(1,1'-dinaphthyl-2.2'-diyl)-*N*-*t*-butyl-*N'*-(*S*)-1-phenylethylphosphoramidite (13).** Purification by column chromatography (SiO_2 pentane/ ether, 50:1, Rf = 0.59) gave 830 mg (58% yield) of **13** as a white foam. $[\alpha]_D$= +401° (c = 0.71, $CHCl_3$); ^{1}H-NMR (300 MHz) δ = 8.04-7.91 (m, 4H), 7.64 (m, 1H), 7.48-7.14 (m, 12H), 4.21 (dd, *J* = 17.0, 3.5 Hz, 1H), 3.69 (d, *J* = 17.0 Hz, 1H), 1.46 (d, *J* = 3.5 Hz, 9H);^{13}C-NMR (200 MHz) δ = 150.5, 150.4, 149.7, 142.4, 142.3, 132.7, 132.6, 131.3, 130.5, 130.1, 130.0, 128.2, 128.1, 127.7, 127.5, 127.0, 125.9, 124.7, 124.4, 122.4, 122.3, 122.1, 121.7, 56.5, 56.1, 45.8, 45.7, 31.7, 31.4; ^{31}P-NMR (200 MHz) δ = 147.6; HRMS calcd for $C_{31}H_{28}NO_2P$ 477.186 found 477.187.

1,2-Benzodioxa-*N,N'*-di-(*S,S*)-1-phenylethylphosphoramidite (14). Purification by column chromatography (SiO_2 hexane/ CH_2Cl_2, 4:1, Rf = 0.70) gave 936 mg (86% yield) of **14** as a colorless crystalline material. $[\alpha]_D$= -264° (c=0.79, $CHCl_3$); ^{1}H-NMR (200 MHz) δ = 7.26-7.14 (m, 12H), 7.01-6.98 (m, 2H), 4.45 (m, 2H), 1.79 (d, 6H); ^{13}C NMR (200 MHz) δ = 146.8, 142.0, 129.1, 127.9, 127.7, 127.6, 126.9, 121.7, 53.3, 53.0, 22.4, 22.2; ^{31}P NMR (200 MHz) δ = 151.78; HRMS calcd for $C_{22}H_{22}NO_2P$ 363.138 found 363.138.

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